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TECHNICAL REPORT

Rational Design and Development of Reactive Multifunctional Micellar Composite Nano-particles for Destruction of Bio-agents

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February 2015

HDTRA1-10-1-0094

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14. ABSTRACT Due to increasing demand of efficient destruction of bio-agent, multi functional composites have been recently investigated for destruction of bio-agents. Their materials have efficient destruction and neutralization of targeted biomolecules (chemical warfare agents, bio-agents, and other toxics) by combined effects of aero-oxidation, electro-oxidation, photo-catalytic oxidation and absorption. Four types of multifunction composites (Au-metal oxide core-shell nanoparticles, , multifunction porous metal oxide-silica composites, porous silicon - Titania and PSi-silver heterojunctions) have been successfully synthesized to meet with the large scale synthesis and efficient co-encapsulation of one or more agents.				
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CONVERSION TABLE

Conversion Factors for U.S. Customary to metric (SI) units of measurement.

MULTIPLY → BY → TO GET
TO GET ← BY ← DIVIDE

angstrom	1.000 000 x E -10	meters (m)
atmosphere (normal)	1.013 25 x E +2	kilo pascal (kPa)
bar	1.000 000 x E +2	kilo pascal (kPa)
barn	1.000 000 x E -28	meter ² (m ²)
British thermal unit (thermochemical)	1.054 350 x E +3	joule (J)
calorie (thermochemical)	4.184 000	joule (J)
cal (thermochemical/cm ²)	4.184 000 x E -2	mega joule/m ² (MJ/m ²)
curie	3.700 000 x E +1	*giga bacquerel (GBq)
degree (angle)	1.745 329 x E -2	radian (rad)
degree Fahrenheit	$t_k = (t^{\circ}f + 459.67) / 1.8$	degree kelvin (K)
electron volt	1.602 19 x E -19	joule (J)
erg	1.000 000 x E -7	joule (J)
erg/second	1.000 000 x E -7	watt (W)
foot	3.048 000 x E -1	meter (m)
foot-pound-force	1.355 818	joule (J)
gallon (U.S. liquid)	3.785 412 x E -3	meter ³ (m ³)
inch	2.540 000 x E -2	meter (m)
jerk	1.000 000 x E +9	joule (J)
joule/kilogram (J/kg) radiation dose absorbed	1.000 000	Gray (Gy)
kilotons	4.183	terajoules
kip (1000 lbf)	4.448 222 x E +3	newton (N)
kip/inch ² (ksi)	6.894 757 x E +3	kilo pascal (kPa)
ktap	1.000 000 x E +2	newton-second/m ² (N-s/m ²)
micron	1.000 000 x E -6	meter (m)
mil	2.540 000 x E -5	meter (m)
mile (international)	1.609 344 x E +3	meter (m)
ounce	2.834 952 x E -2	kilogram (kg)
pound-force (lbs avoirdupois)	4.448 222	newton (N)
pound-force inch	1.129 848 x E -1	newton-meter (N-m)
pound-force/inch	1.751 268 x E +2	newton/meter (N/m)
pound-force/foot ²	4.788 026 x E -2	kilo pascal (kPa)
pound-force/inch ² (psi)	6.894 757	kilo pascal (kPa)
pound-mass (lbm avoirdupois)	4.535 924 x E -1	kilogram (kg)
pound-mass-foot ² (moment of inertia)	4.214 011 x E -2	kilogram-meter ² (kg-m ²)
pound-mass/foot ³	1.601 846 x E +1	kilogram-meter ³ (kg/m ³)
rad (radiation dose absorbed)	1.000 000 x E -2	**Gray (Gy)
roentgen	2.579 760 x E -4	coulomb/kilogram (C/kg)
shake	1.000 000 x E -8	second (s)
slug	1.459 390 x E +1	kilogram (kg)
torr (mm Hg, 0° C)	1.333 22 x E -1	kilo pascal (kPa)

*The bacquerel (Bq) is the SI unit of radioactivity; 1 Bq = 1 event/s.

**The Gray (GY) is the SI unit of absorbed radiation.

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PI Name: Donghai Wang

Organization/Institution: Department of Mechanical and Nuclear

Engineering, Pennsylvania State University

Project Title: Rational Design and Development of Reactive

Multifunctional Micellar Composite Nano-particles for

Destruction of Bio-agents

Abstract

Due to increasing demand of efficient destruction of bio-agent, multifunctional composites have been recently investigated for destruction of bio-agents. These materials have efficient destruction and neutralization of targeted biomolecules (chemical warfare agents, bio-agents, and other toxics) by combined effects of aero-oxidation, electro-oxidation, photo-catalytic oxidation and absorption. Four types of multifunctional composites (Au-metal oxide core-shell nanoparticles, multifunctional porous metal oxide-silica composites, porous silicon -Titania and P-Si-silver heterojunctions) have been successfully synthesized to meet with the large-scale synthesis and efficient co-encapsulation of one or more agents.

Objectives

The objective of this research is:

1. To develop new efficient bio-agent neutralizer or destructor based on multifunctional composite nanoparticles in large scale.
2. To gain a fundamental understanding of the basic science of how structure, surface chemistry, and catalytic species affect chemical absorption and deactivation of bio-agents by dissecting structure-property-performance relationships of these materials and by understanding their synthesis and resulting structure and composition of the materials.

Due to increasing demand of efficient destruction of bio-agent, multifunctional composite have been recently investigated for destruction of bio-agents. These materials' unique properties at the nano scale, including their abrasive character and high surface area leading to very close contact with cells, and their unusual surface morphology leading to high surface reactivity, make them promising biocides. Nanoparticles can also be prepared in a variety of forms, such as powders, slurries, pellets, and membranes, making them more convenient and widely applicable

for bio-agent destruction. Additionally, nanoparticles can generally be easily stored, which increases their flexibility. Although the metal oxide nanoparticles perform well in destruct vegetative bacterial, the reactivity of the pure metal oxide nanoparticles may not be strong enough to destruct non-vegetative bacterial (e.g., spores) which would be more vulnerable to additional attack. Therefore, formation of efficient agents for destruction of bio-agents necessitates incorporating strong conventional biocides that synergistically function with metal oxide nanoparticles. This concept becomes very important in the case of spores, where a combination of two agents is usually much more efficient than one agent alone, and very often necessary. Ideal nanoparticle-based biocides should be equipped with desirable multi functionality including 1) the ability to deliver large amounts of biocides, 2) efficient co-encapsulation of one or more agents and 3) reactive or energetic destruction of bio-agents.

At the very beginning, we developed a micellar Au-metal oxide core-shell nanoparticles (Au-SiO₂-Polymer) and silicon (Si) nanoparticle with long term stability of micelles with high loading of organic compound through the cross-link and lock in the micellar structures by polymerization of the reactive functional group. Despite of good stability, structural property and expected good biocide performance of the materials (Au-SiO₂-Polymer and Si nanoparticle), only limited amount was synthesized so that the materials were hardly applied to mass application. It is required to produce material in the scalable manner.

Then as schematically illustrated in **Figure 1**, the reactive and multifunctional porous metal oxide-silica composite nanoparticles (ZnO-SiO₂ nanoparticles) were developed for efficient destruction or neutralization of targeted biomolecules (chemical warfare agents, bio-agents, and other toxics) by aero-oxidation, electro-oxidation, or photo-catalytic oxidation. In the composite nanoparticles, metal oxides cross-link surfactant or polymer into core-shell micellar composite nanoparticles. The surface of the porous silica is covalently bonded with an organic functional group through silane chemistry.

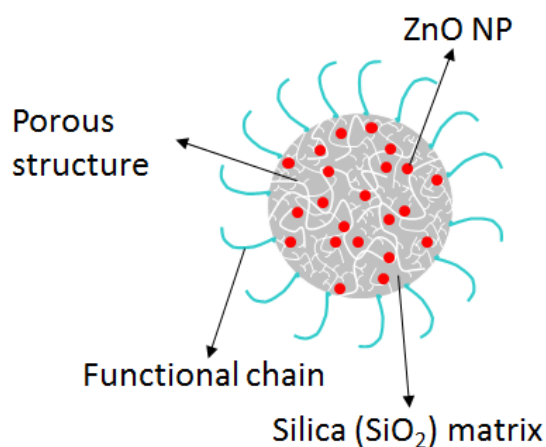


Figure 1. A scheme of multifunctional metal oxide (ZnO)-silica composite nanoparticles for destruction of bio-agents

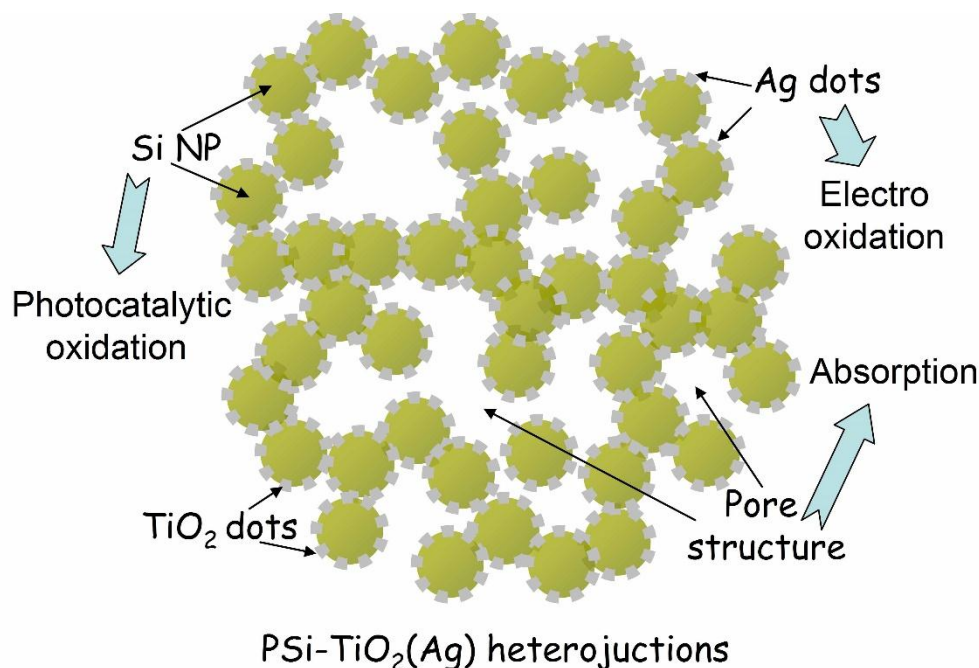


Figure 2. A scheme of multifunctional porous silicon (PSi)-Titania (TiO₂) or PSi-silver (Ag) heterojunctions for destruction of bio-agents.

Finally, reactive and multifunctional porous silicon (PSi)-Titania (TiO₂) or PSi-silver (Ag) heterojunctions were developed. These materials have efficient destruction and neutralization of targeted biomolecules (chemical warfare agents, bio-agents, and other toxics) by combined effects of aero-oxidation, electro-oxidation, photo-catalytic oxidation and absorption. As schematically illustrated in **Figure 2**, the reactive and multifunctional porous silicon (PSi)-Titania (TiO₂) or PSi-silver (Ag) heterojunctions were synthesized. In the composite nanoparticles, Titania and/or silver nanodots dispersed on the surface of silicon particles instead of core-shell structure to utilize mass transmission.

Accomplishments

In this project, we focused on synthesis and characterization of multifunctional composite nanoparticles, such as micellar Au-metal oxide core-shell nanoparticles, metal oxide (ZnO)-silica composite nanoparticles, porous silicon (PSi)-Titania (TiO₂) and PSi-silver (Ag) heterojunctions.

1. Multifunctional micellar Au-metal oxide core-shell nanoparticles

Micellar Au-metal oxide core-shell nanoparticles were synthesized based on a controlled cross-link of the metal oxide precursor on the hydrophilic head group of the surfactant and block copolymer by using typical sol-gel synthesis methods. Organosilanes (such as: 3-Aminopropyltrimethoxysilane, 3-Mercaptopropyltriethoxysilane) were successfully attached to the metal oxide surface through either a post-synthesis grafting technique or a direct co-condensation technique. Moreover, these chelating functional ligands (e.g., thiols) could stabilize the Au molecular precursor so as to produce sub-nanometer Au clusters coupled with metal oxide supports. So far, several types of multifunctional composite nanoparticles (NPs) were successfully synthesized.

(1) Micellar Au-SiO₂-F127 composite NPs

We have successfully used the polymeric surfactant (pluronic F127: PEO-PPO-PEO) to direct formation of the self-assembled micellar Au-SiO₂-F127 composite NPs. Firstly, F127 self-assemble into micellar structures, the functional silicate precursors hydrolyze and condense at the hydrophilic shell (PEO) region, followed by self-assembly of sub-nanometer Au clusters in the core or shell regions.

(2) Au-SiO₂-CTACl composite NPs

In addition to amphiphilic block polymers, we also used a typical cationic surfactant (hexadecyltrimethylammonium chloride, CTACl) as a template to prepare thiol-functionalized mesoporous silica particles, which were then used as precursors for the synthesis of Au-SiO₂-CTACl composite NPs. In this approach, stable colloidal suspensions of thiol-functionalized mesoporous silica particles of defined sizes were first prepared by a co-condensation route using triethanolamine (TEA) as the base catalyst and the surfactant of hexadecyltrimethylammonium chloride (CTACl) as a template. Then, a certain amount of Au colloidal solution was added into the above thiol-functionalized mesoporous silica suspension. Due to the interaction between thiol groups and Au, the Au clusters were assembled onto the mesoporous SiO₂ particles to form Au-SiO₂-CTACl composite NPs.

(3) Mesoporous Au-TiO₂-P123 composite NPs

Composite Au-TiO₂ has been demonstrated as an efficient photo catalyst, which can be used to conduct photo degradation of bio-agents along with aero-oxidation. To homogenously embed gold nanoparticles within the titania framework, we have developed a multicomponent assembly approach, where surfactant, titania, and gold building clusters were cooperatively assembled in a one-step process.

(4) Si-graphene composite NPs

Electro oxidation is another efficient approach for destruction of bio-agents. However, the composite nanoparticle is an insulating material. When it is loaded on conductive carbon, the agglomeration prevents the composite nanoparticle from functioning as single nanoparticle. To synergistically utilize both catalytic properties of nanoparticles and high conductivity of carbon, we have used highly conductive, high-surface-area graphene to assemble silicon nanoparticle into a controlled structure potentially used for destruction of bio-agents. Si-graphene composite NPs were prepared by a one-step process through solution reduction of SiCl₄ and graphene oxide simultaneously using alkaline metal. Graphene oxide was prepared from graphite by using an oxidation-reduction wet-chemistry approach.

2. Multifunctional metal oxide (ZnO)-silica composite nanoparticles

Development of the efficient and high performance biocide nanomaterial can contribute to reduce the threat, especially from the chemical and biological threats. Since wide application of the material only achieved by making the material in large scale, it is crucial to develop the large scale synthesis way for the multifunctional composite capable of catalytic destruction and of absorption and deactivation of bio-agents by controlling their composition, interfacial chemistry and nanostructure. There is much interest in the large scale synthesis of nano-sized particle for biocide application. We developed novel way to produce of robust biocides of porous metal oxide (ZnO)-silica (SiO₂) composite and SiO_x nanoparticles in large scale by 1) combination of controlled self-assembly and aerosol-assisted process (porous metal oxide-silica composite nanoparticles) or by 2) alkali metal based reduction based synthesis (SiO_x nanoparticle).

The scale of production is several grams per a batch of synthesis. Especially, the continuous aerosol process enables large synthesis of nanomaterial for biocide application. The structure, composition and morphology of the material were confirmed by various methods. It is very useful to apply those materials for biocide since they have abrasive character, high surface area and unusual surface morphology with high surface reactivity. For instance, the nano porous $\text{ZnO}_x\text{-SiO}_{2(1-x)}$ composite, SiO_2 serves as porous and inert matrix which can absorb conventional biocides in the pore, while embedded metal oxides (ZnO) nanoparticles serve as catalytic oxidative component for destruction of bio-agents by aero-oxidation, electro-oxidation, or photocatalytic oxidation. SiO_x nanoparticles were synthesized in large scale where SiO_x nanoparticle can absorb conventional biocides and can be used for the destruction of non-vegetative bacterial cells and vegetative bacterial cells.

In this context, multifunctional nanoparticle-based biocides such as metal oxide-halogen adducts have been studied, where metal oxide serve as the carrier for a halogen biocide to form a composite showing efficient performance at destruction of bio-agents. In the metal oxide-based adducts, biocides can only be attached to the particle surface, thus limiting the loading capacity and the flexibility to protect and release the biocides at targeted sites in bio-agent.

By controlling the composition, interfacial chemistry and nanostructure of the metal oxide-silica composite and SiO_x nanoparticle, we can understand the principles of 1) catalytic oxidative destruction and 2) absorption and deactivation of bio-agents by multifunctional composite nanoparticles. In addition, the large synthesis of material allows practical application of the synthesized novel nanomaterial as biocides towards various types of bio-agents. The basic study carried in this research can provide the insight for the design of advanced materials for sensing, protecting and securing chemical warfare agents, bio-agents and toxic industrial materials thereby largely enhance the efficiency of the warfighter as well as civilian under the potential threat of such attack. The research facilitates further understanding of the principles of multifunctional composite nanoparticles for absorption and deactivation of bio-agents and also provides novel knowledge to design advanced materials for sensing, protecting and securing chemical warfare agents, bio-agents and toxic industrial materials. In the future, current research can be further extended and applied for the protection of the warfighter and civilians from different types of biologically hazard agents.

3. Multifunctional porous Si-TiO₂(Ag) heterojunctions

In order to prepare robust biocides PSi-TiO₂(Ag) heterojunctions, we developed a novel way to produce porous silicon with large surface area. PSi-TiO₂ and PSi-Ag heterojunctions were then obtained by a sol-gel assistant modification process and photocatalytic-reduction process, respectively. It is very useful to apply those materials for biocide since they have abrasive character, high surface area and unusual surface morphology with high surface reactivity. For instance, the PSi-TiO₂ heterojunctions, the mesopore silicon with a surface area up to $580 \text{ m}^2 \text{ g}^{-1}$ serves as porous and inert matrix which can absorb conventional biocides in the pore, while dispersed TiO₂ nanoparticles, their self and the heterostructures serve as catalytic oxidative component for destruction of bio-agents by aero-oxidation, electro-oxidation, or photocatalytic oxidation. And the self-built field derived from the band structure of PSi-TiO₂ heterostructures can facilitate the photo-generated charge separation and enhance the photocatalytic oxidation. In the PSi-Ag heterojunctions, Ag can not only act as time-honored antibacterial agent since thousands years ago for its tightly absorption on the

bacterial cells and the protein coagulation properties, but also can improve the photocatalytic activity of silicon through inhibiting the recombination of photogenerated charge pairs by establishing Schottky barriers and the surface plasmon resonance of Ag.

(1) Porous Si

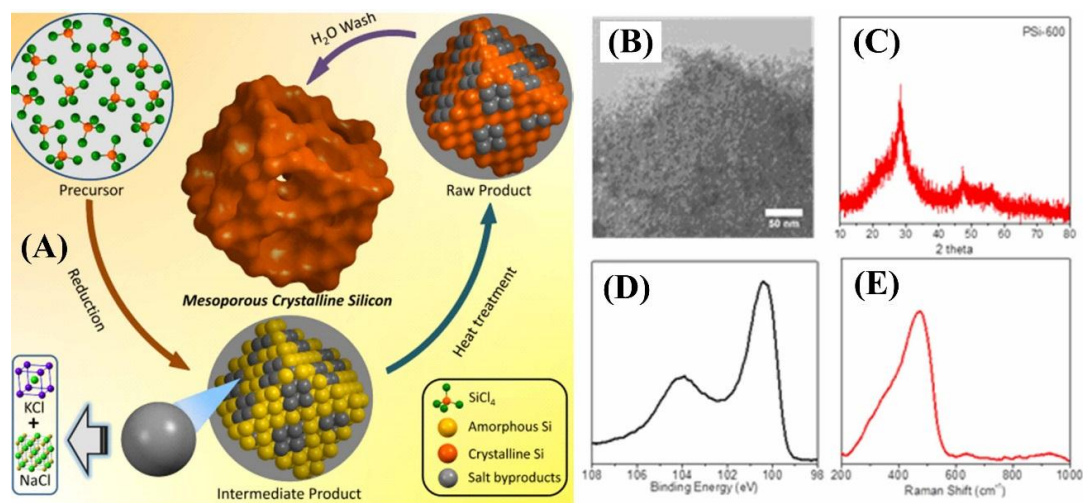


Figure 3. Scheme of the synthesis route of mesopore crystalline Si (A) and Characterizations of mPSi(A, TEM image; B, XRD pattern; C, XPS spectrum of Si2p; D, Raman spectrum).

We designed a synthesis route (Figure 2A) based on a modified SiCl_4 reduction utilizing salt byproducts as self-forming templates. The employing the alkaline alloy NaK as the reducing agent leads to formation of amorphous Si particles under ambient conditions. Due to their poor solubility in the solvent, the simultaneously-formed salt byproducts and Si precipitate out, forming a solid matrix. The amorphous Si crystallizes into a framework composed of interconnected primary particles during the following heat treatment, with its growth being restricted by the salt. Similarly, the salt templates are also restricted by the Si network and thus have mostly uniform size. The material is then washed with water to remove the salt byproducts, generating the final porous Si. The resulting materials were then characterized. The mPSi sample was studied first. The TEM image in Figure 2B clearly shows that the mPSi has a disordered mesopore structure with a Si framework consisting of interconnected primary particles with an average size of about 5 to 10 nm. The diffraction peaks in the XRD pattern of mPSi are assigned as crystalline Si (Figure 2C, JCPDS Card No.27-1402). The X-ray photoelectron spectrum (XPS) has peaks appearing around 100 eV and 104 eV, which are assigned to Si (0) and Si (+4), respectively (Figure 2D). The binding energies in between correspond to SiO_x ($0 < x < 2$). The appearance of the surface oxides, which is commonly observed in Si nanoparticles, is also verified by the Raman spectrum (Figure 2E), in which a peak shoulder appears around 350 cm^{-1} and is attributed to amorphous SiO_x ($0 < x < 2$) and SiO_2 . Nitrogen sorption analysis was also conducted for the mPSi sample, which indicates the presence of mesopore structure with a BET specific surface area of $497 \text{ m}^2 \text{ g}^{-1}$ and the pore size distribution is centered around 10 nm. For the oxide layer is harmful to the photo-generated charge separation and migration, HF treatment was performed to remove the surface oxide before using for prepare composite. After modification, the surface area of the mesopore silicon materials is up to $580 \text{ m}^2 \text{ g}^{-1}$ and show a remarkable

photocatalytic activity. Furthermore, the pore size, primary particle size, and surface area may be tuned by adjusting the heat treatment temperature to control the crystal growth.

(2) Porous Si@TiO₂ heterojunctions

Heterojunctions of two semiconductors with matched band structure can produce a self-built field to facilitate the photo-generated charge separation and enhance the photocatalytic antibacterial activity. If the heterojunctions with a core/shell structure usually have a good activity in the initial for the actions of the self-built field of band structures (Figure 3 up). For the photo-generated holes will concentrated in the core and cannot be well consumed, the band structure of semiconductor in the core will changed and cannot keep the self-built field. That means only the semiconductor in the shell can play actions. By comparison, because the semiconductor in the core of a core/dots structure is also exposed on the surface, the photo-generated holes can be easily consumed to avoid change the band structure. As a result, heterojunctions with core/dots structures can keep its activity in long term.

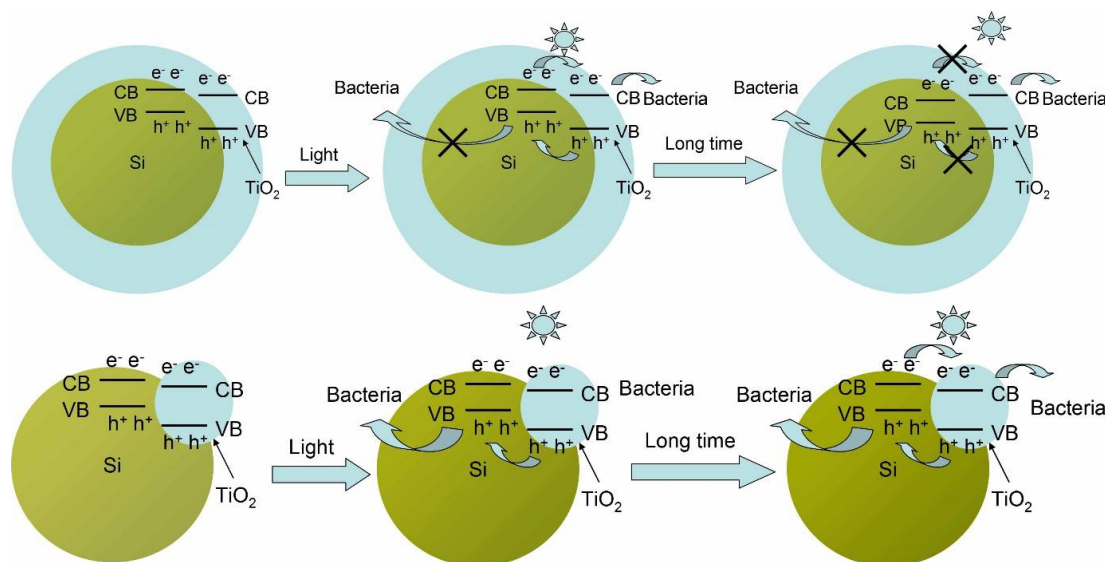


Figure 4. Comparison of the photocatalytic antibacterial activity between core/shell structure and core/dots structure.

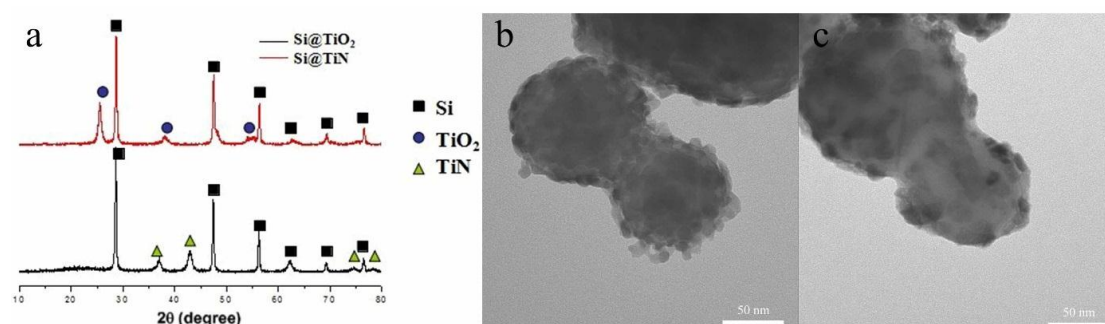


Figure 5. XRD patterns (a) and TEM images (b, Si@TiO₂; c, Si@TiN) of products obtained at different annealing temperature of Si@ amorphous TiO₂ synthesized via sol-gel process.

Si@TiO₂ heterojunctions with core/dots structures were synthesized by a sol-gel process combined with annealing process by using commercial nano silicon as starting materials.

Figure 4 a shows the XRD pattern of obtained TiO_2/Si heterojunctions, the narrow characteristic silicon diffraction peaks at 28.4° , 47.3° , and 56.0° are derived from Si nanoparticles, while the peaks centered at 25.4° , 38.1° , and 54.4° indicate the formation of well crystalline anatase phase TiO_2 . TEM image of the heterojunctions reveals the core/dots structure, TiO_2 nanodots with a size about 5 nm are uniform dispersed on the surface of Silicon nanoparticles. TiN is a gold color semiconductor, in which the Ti(III) is not a stable valence state of Ti. Si@TiN heterojunctions also can be prepared by increasing the annealing temperature under reduction atmosphere. The XRD pattern indicate the formation of TiN (Figure 6a) and the core/dots structure is confirmed by the TEM (Figure 6c). By using this method, PSi@ TiO_2 and PSi@TiN have also been fabricated by using our synthesized porous silicon as starting materials. These heterojunctions, the mesopore silicon with a surface area up to $580 \text{ m}^2 \text{ g}^{-1}$ serves as porous and inert matrix which can absorb conventional biocides in the pore, while dispersed TiO_2/TiN nanoparticles, their self and the heterostructures serve as catalytic oxidative component for destruction of bio-agents by aero-oxidation, electro-oxidation, or photocatalytic oxidation. The unstable valence state of Ti in the TiN will also helpful for destruction of bio-agents. And the self-built field derived from the band structure of PSi- TiO_2 heterostructures can facilitate the photo-generated charge separation and enhance the photocatalytic oxidation.

(3) Porous Si@Ag heterojunctions

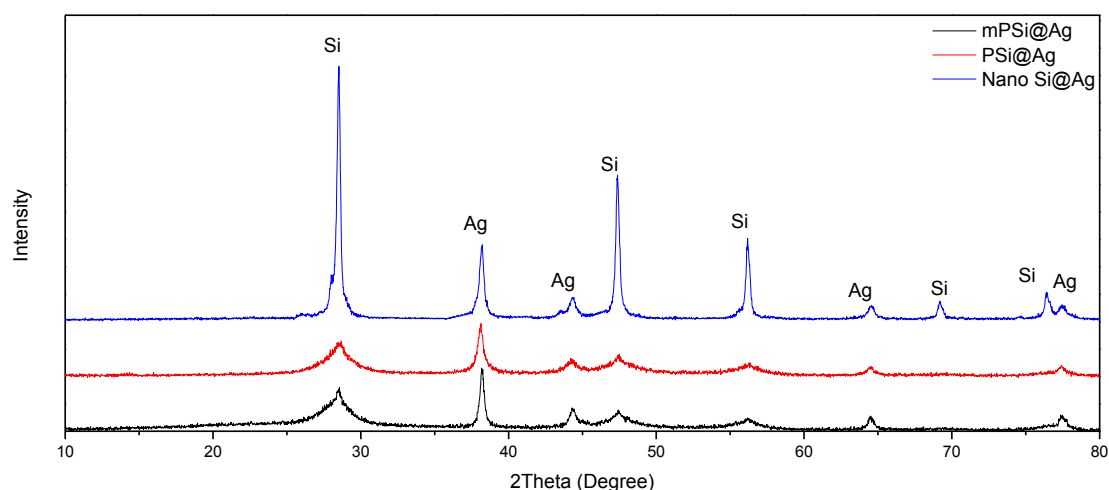


Figure 6. XRD patterns of different silicon/silver heterojunctions prepared by photocatalytic loading process.

Silver is considered to be time-honored antibacterial agent since thousands years ago for its tightly absorption on the bacterial cells and the protein coagulation properties. Nowadays, people found when the size of silver is reduced to quantum size it will have strong plasmon phenomenon and become plasmonic metal. The surface plasmon resonance of Silver can enable efficient charge transfer. The establishing Schottky barriers created by metal (Ag) and semiconductor are also beneficial to the charge transfer process. In this aim, we designed a porous silicon @ silver heterojunctions based on commercial Si nanoparticles and our synthesized porous silicon. The Si@Ag heterojunctions were carried out via a photocatalytic reduction process by utilizing the photo-generated electrons of silicon. Figure 5 shows the

XRD patterns of different Si@Ag heterojunctions prepared from different types of silicon. The narrow characteristic silicon diffraction peaks at 28.4° , 47.3° and 56.0° are derived from Si; the peaks centered at 38.1° , 44.4° , 64.5° and 77.4° reveal the formation of nano-sized silver. The particle size of silver can be easily tuned by adjusting the concentration of AgNO_3 , irradiation time and intensity. Porous Si@Ag heterojunctions can combined the nature antibacterial activities of Silver with the plasmonic enhanced photocatalytic biocide of Si@Ag heterojunctions, as well as the absorption properties derived from the pore structure and large surface area of porous silicon.

Based on the point of combined nature antibacterial activities and photocatalytic actions for efficient destruction or neutralization of targeted biomolecules (chemical warfare agents, bio-agents, and other toxics), $\text{Bi}_2\text{O}_2\text{CO}_3@\text{Bi}_2\text{S}_3$, $\text{Bi}_2\text{O}_3@\text{Bi}_2\text{S}_3$, $\text{BiVO}_4@\text{Bi}_2\text{S}_3$ and $\text{BiVO}_4@\text{Ag}$, etc Bi based heterojunctions, and $\text{Cu}_2\text{O}@\text{TiO}_2$, $\text{Cu}_2\text{S}@\text{TiO}_2$, $\text{Cu}_2\text{O}@\text{Ag}$, $\text{Cu}_2\text{S}@\text{Ag}$, $\text{CuInS}_2@\text{TiO}_2$, $\text{CCuInS}_2@\text{Ag}$, etc Cu based heterojunctions are also designed and in preparation.

In this context, multifunctional nanoparticle-based biocides such as porous Si@ TiO_2 or Ag heterojunctions have been studied, where porous silicon serve as the carrier for Silver or titania biocide to form a heterojunctions showing efficient performance at destruction of bio-agents by cooperative effect. In the porous Si-based heterojunctions, biocides can not only be attached to the particle surface, but also in the pore structure to increase loading capacity and the flexibility to protect and release the biocides at targeted sites in bio-agent.

Resulting Publication

Journal Publications:

1. Fang Dai, Jiantao Zai, Ran Yi, Mikhail L. Gordin, Hiesang Sohn, Shuru Chen and Donghai Wang, Bottom-up Synthesis of Mesoporous Crystalline Silicon with High Surface Area and Superior Hydrogen Evolution Performance, Nature Communication (In revision).
2. Jiantao Zai, Ran Yi, Fang Dai, Donghai Wang, Doping effect on the selectivity of photoreduction of CO_2 by using mesoporous porous Si as photocatalysts. (In preparation)
3. Jiantao Zai, Fang Dai, Ran Yi, Donghai Wang, Rational synthesis of B-doped mesoporous crystalline silicon and its application on CO_2 photoreduction. (In preparation)

Presentations:

1. Wang, D. H. Bottom-up Synthesis and Self-Assembly of Nanoporous Crystalline Semiconductors, In International Conference on Nanoscience and Technology, Beijing, China, September 2013.
2. Gordin, M. L., Chen, Z., Xu, T., Wang, D. Synthesis and Characterization of Ordered Mesoporous Metal Oxide-Carbon Nanocomposites and Their Applications in Supercapacitors. 241st American Chemical Society (ACS) National Meeting, Anaheim, CA, 2011.